D1.14: Remediation Techniques for "special" contaminants

POTENTIAL OF ACTIVATED CARBON TO RECOVER RANDOMLY-METHYLATED-B-CYCLODEXTRIN SOLUTION FROM WASTE WATER ORIGINATING FROM *IN SITU* SOIL FLUSHING

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Introduction

Cyclodextrins (CD) are enzymatically produced from starch by bacteria and consist of 6-8 (α-1,4)-linked glucopyranose molecules with both an apolar cavity and polar exterior. Because of their structure CD are able to encapsulate apolar molecules and therefore enhancing their water solubility. In addition, because of its low toxicity and high biodegradability, CD are highly suitable for a broad range of applications in the pharmaceutical industry, food industry, cosmetics, agricultural industry and chemical industry (Del Valle, 2004). Another potential application of CD is to accelerate the clean-up of soils by bioremediation or in-situ soil flushing. By enhancing the water solubility, apolar contaminants are more available for biodegradation (Gan, 2009; McCray, 2000) and/or are more efficiently removed from the soil (Berselli, 2006). Consequently, CD can significantly reduce the treatment time. A lot of research has been performed to accelerate the treatment of soils by the time-consuming pump and treat method to cleanup soils contaminated with apolar contaminants using chemical solubility enhancers such as cosolvent (Kosaric 2001) and surfactants (Svab et al., 2009; Zhou and Zhu, 2007). However, because of the toxicity and persistence of these chemicals, biosurfactants (Berselli et al., 2006) or CD are preferably used. A lot of results have been published regarding the enhancement of the water solubility and/or bioavailability with CD for contaminants such as PCB (Balogh, 2007), trichloroethylene (Fenyvesi et al. 2010), polycyclic aromatic hydrocarbons (Viglianti, 2006; Wang, 2003) and pesticides (Morillo et al. 2001, Wong 2010). In addition some field trials to test soil flushing with CD which obtained good results have been published (Boving, 1998; McCray and Brusseau, 1998).

Although the overall high observed efficacy, for now the practical use is limited because of the high costs of CD and high concentrations needed to significantly reduce the treatment time. CD concentrations used to achieve a significant improved desorption in field trials are situated between 1.5% (w/v) and 10% (w/v) (Boving, 1998; Leitgib, 2008). A high recovery of the CD from the waste water would reduce the costs and makes the technique also economically interesting for the industry to apply. Boving et al. (1998) already emphasized the importance of reusing CD to make soil flushing viable. For the volatile contaminants such as PCE and TCE they tested the removal of these contaminants from CD solution by air stripping. Alternative methods are required for less volatile contaminants.

The current study proposes the use of active carbon (AC) to treat waste water from soil flushing with CD in order to selectively separate hydrocarbons from wash water containing CD. Therefore, an AC with minimal sorption capacity for CD is needed. Until now, only Kania et al. (2012) looked into the adsorption of CD to AC and were able to establish adsorption isotherms. Moreover, it seemed that the type of CD affected the dispersion of AC in water (Kania, 2012). More research regarding the possibilities of reusing CD by AC is essential, which is the scope of this article. Earlier studies of different authors (including our own bioremediation studies) designate randomly-methylated-β-

cyclodextrin as a potential *in situ* solubiliser because of its relative high half-life time (1 to 2 years, Fenyvesi, 2005) and relative low cost (Fava, 2002). In addition, a lot of good results have been obtained with this CD to enhance the bioavailability or bioremediation of soils contaminated with hydrocarbons (Molnar, 2002; Molnar, 2005).
The present study aimed to investigate whether CD can pass through the active carbon filter without reducing the CD concentration when the contaminated waste water is treated and whether the presence of CD negatively affects the purification step to remove the organic pollutants from the pumped soil water with activated carbon. More specifically, this paper tries to answer the following questions: (i) how many CD is lost by sorption to activated carbon, (ii) which type of activated carbon results in the minimal loss of CD, (iii) does the amount of CD sorbed to AC depends on the CD concentration in the water, (iv) does the presence of MO in the water affects the amount of CD sorbed to AC, (v) does the presence of CD in the flushing water affects the removal efficiency AC for MO and finally (vi) how much CD is lost by sorption to the soil and AC during the pump and treat technology? Only when these imposed questions are answered, we will be able to estimate the applicability of CD in the field.

Materials and Methods

To answer the six questions, three types of adsorption batch experiments and one lab-scale soil flushing experiment were performed. Each experiment was performed in triplicate. The CD randomly-methylated-β-cyclodextrin was obtained from Wacker Chemie (Germany, technical grade). In the first batch experiment, the capacity of four different types of activated carbon originating from Desotec (AC-A, AC-B, AC-C and AC-D) were tested to adsorb CD. Adsorption experiments with CD were performed in 250 mL flasks containing 1 g of CD in 100 mL tap water. Granular AC was grinded to powder and particles smaller than 63 µm were used for the adsorption experiments. The activated carbon was added in different concentrations to the solution, i.e. 0, 0.1, 1.0, 2.0, 5.0 or 10 g/L. After 4 hours on a magnetic stir plate, the water was filtrated over 0.45 µm filter and the filter was washed with 100 mL of clean tap water. The remaining concentration of CD in the water was measured with HPLC-ELSD (40 °C, 3.5 bar) using a RP-18 column (5 µm, 125 mm x 4 mm) and a mobile phase containing 75%:25% Acetonitrile:H_2O at 1 mL/min.

A second batch experiment with AC-C and AC-D was performed to test whether the adsorption of CD depends on the concentration of CD in the solution. Powdered granular AC (10 g/L) was added to 100 mL tap water containing different concentrations of CD ranging between 0 and 50 g/L. After 4 hours of shaking and sequentially filtering and washing, the remaining concentration of CD in the water was measured.
AC-B and AC-C were also used in a third batch experiment to test whether the presence of MO increases the adsorption of CD by AC. Therefore 10 g of AC was added to 1000 mL of tap water containing 1 mg/L dissolved MO and 10 g/L of CD solution and treated as in the previous experiment. Finally, a column experiment was set-up to measure both the amount of CD sorbing to the soil and to a column of AC. Eight glass columns (Ø 5 cm x 30 cm) were filled with 500 g of soil (wet weight) containing 4220 mg MO/kg DW. Two columns (ctr 1 and ctr 2) were flushed with pure tap water. The other six columns were flushed with 20 g L^{-1} CD solution. The water was pumped from the bottom up at 10 mL/h in cycli of 8.5 h, followed by a period of 3.5 h with the pump turned off to increase the contact time between CD and the soil. That way 1.5 pore volume was flushed through the soil twice a day. For columns A, B and C, the water was collected in glass bottles and weekly analyzed to determine the MO concentration with GC-FID and the CD concentration with HPLC-ELSD. The water originating from columns D-AC, E-AC and F-AC was conducted over an AC filter (2 cm x 25 cm) filled with AC-C. The concentration CD and MO were monitored for 3 weeks (21 days).

Results

Capacity of different types of active carbon to adsorb cyclodextrin

As is shown in Figure 1, AC-A and AC-D retained a significant amount of CD and decreased the concentration of CD in the water with 88 and 22%, respectively when 10 g/L AC was used. However, at decreasing concentration of CD, less CD was removed from the water and no CD was removed from the water with 1 g/L AC for both types of AC. AC-B and AC-C gave better results, since approximately 100% recovery of CD could be obtained from the water until 10 g/L of AC.

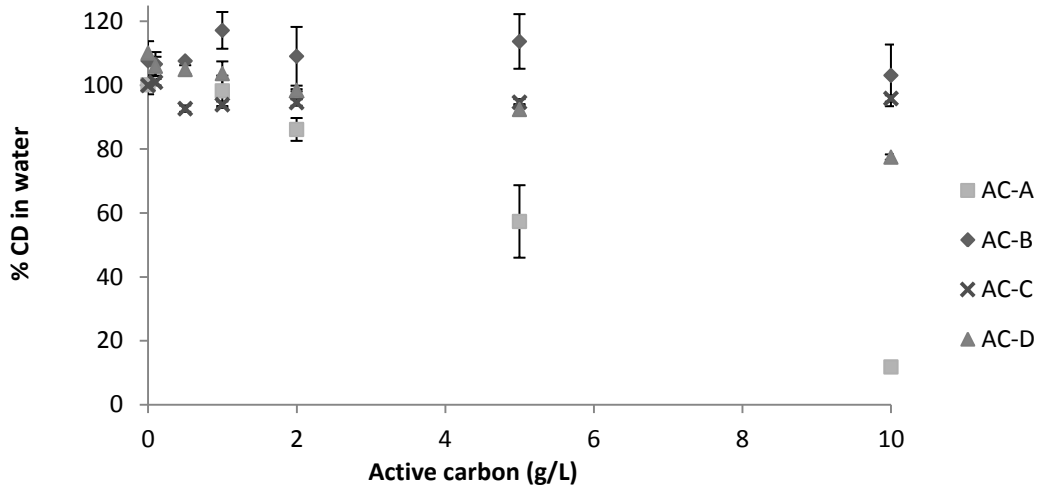

Figure 1: The sorption capacity of different types of active carbon for cyclodextrin at different concentrations of active carbon. The error bars give the standard deviation of triplicates.

The effect of CD concentration and mineral oil on the CD adsorption capacity of active carbon

From the previous results AC-B and AC-C were selected for further examination. It was tested whether the concentration of CD would increase the sorption of CD on these AC. As is shown in Figure 2, lowering or increasing the concentration of CD in the water did not affect the sorption of CD to AC-C. However, more CD was retained by AC-B, when higher concentrations of CD were used. Only 65% of the added 50 g/L CD could be recovered from the water with 10 g/L of AC-B. At lower concentrations of CD (2 or 10 g/L) no significant losses of CD were observed with the same AC-B.

Since the CD-MO complex might adsorb to the AC, which can result in higher losses of CD, it was tested whether more CD is removed by AC, when MO is present in the water. Figure 3 shows the remaining CD in the water, where it seems that the presence of low concentrations of MO (2 mg/L) in the water do not cause significant losses of CD to AC-C or AC-B.

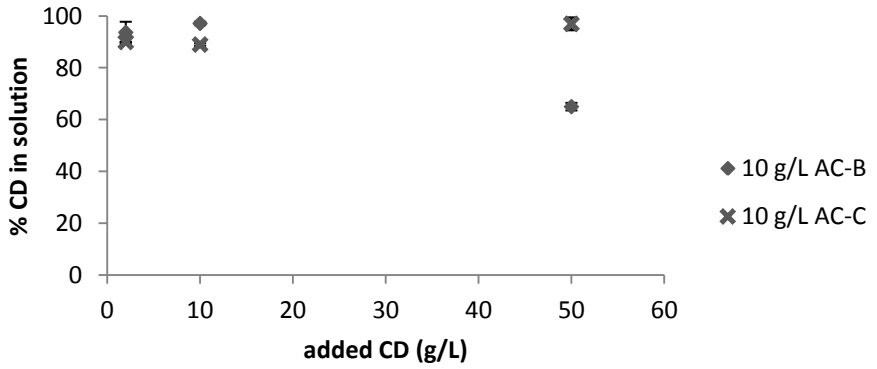

Figure 2: Effect of the cyclodextrin concentration (2, 10 and 50 g/L) on the sorption of cyclodextrin to two types of active carbon (AC-B and AC-C). The error bars give the standard deviation of triplicates.

Losses of CD during soil flushing assays

Based on the previous results, AC-C gave the best result to reuse the cyclodextrin flushing solution after treating the contaminated waste water and was therefore selected for the soil flushing assay. In the column experiment, realistic soil flushing conditions were simulated to investigate the effect on the removal efficiency of MO by AC-C and the recovery efficiency of CD for reuse. More specifically, the effect of high concentrations of MO in the water and the presence of other organic compounds flushed from the soil due to the presence of CD were examined.

Table 1 gives on overview of the average concentration of MO found in the effluent, the total amount of MO flushed from the soil and the percentage of the initial amount of MO which is removed from the soil. After 3 weeks, a significant high amount of MO, varying between 3.9 and 5.1 % of the initial amount of MO in the soil was removed when using 20 g/L of CD solution. After the same period of time, less than 0.05% was washed away with pure tap water.
More interestingly, no significant losses of CD to the soil (average recovery of 97.5%) or to the AC (average recovery of 98.5 %) occurred. Initially, high concentrations of MO were found in the effluent from columns E-AC, F-AC and D-AC. However, a leak occurred in the AC filter causing effluent water from the soil column to leak directly into the effluent bottle without being conducted over the AC filter. As a result elevated MO concentration occurred in the effluent during 21 days, which are not shown in the table. After solving the problem with the filter, the soil flushing assay was prolonged for one week. In this period, MO concentrations as high as 36 700 µg/L (data not shown) were found in the soil extract from columns A, B and C and only 6 % of this amount was found in the effluent of columns D-AC, E-AC and F-AC. This indicates that 94 % of the MO could be removed by the AC filter. Although this treated waste water still contained relative high concentrations of MO (approximately 2130 µg/L), it is uncertain whether this is due to the presence of CD in the water or it is an acceptable value, since the removal efficiency of AC at high concentrations of MO could not be tested without CD.

Table 1: Total amount of mineral oil flushed from the soil columns after 21 days and the average amount of cyclodextrin recovered after flushing (columns A, B and C) or subsequent flushing and treatment of the waste water with active carbon (AC-C) (columns D-AC, E-AC, F-AC).

Column	Average MO concentration in effluent (µg/L)	Total amount of MO flushed (µg)	% MO flushed	CD added (g/L)	% CD in effluent
ctr 1	105	298	0.0	0	< DL
ctr 2	109	320	0.0	0	< DL
A	39567	107687	5.1	20	97
B	36800	81967	3.9	20	97
C	36600	86769	4.1	20	98
D-AC	***	NR	NR	20	98
E-AC	***	NR	NR	20	99
F-AC	***	NR	NR	20	98

*** no accurate data available; NR: not relevant; < DL : value below detection limit

Conclusion

This study shows promising results when using the appropriate AC to recover CD solutions from waste water originating from *in situ* soil flushing. This is important to make this technique economically interesting. However, further experiments are recommended to test whether or not the presence of CD negatively affects the removal of mineral oil from the water. In addition, in field trials the amount of CD will probably not be completely recovered from the soil due to the heterogeneity of the subsoil. Furthermore, the CD concentration in the pumped water will be significantly decreased due to the dilution effect of the soil water pumped from the environment. Results from other flushing experiments (own data, unpublished) showed that high concentrations of CD solutions are required to achieve a high removal efficiency within a reasonable time. Therefore, it will be necessary to concentrate the pumped water to increase the CD concentration to a suitable level after cleaning the waste water with AC.

References

Astray G., Gonzalez-Barreiro C., Mejuto J.C., Rial-Otero R., Simal-Ga´ndara J. A review on the use of cyclodextrins in food. *Food Hydrocolloid*, **2009**, 23, 1631-1640.

Balogh K., Szaniszlo N., H-Otta K., and Fenyvesi E. Can cyclodextrins really improve the selectivity of extraction of BTEX compounds? *Journal of Inclusion Phenomena and Macrocyclic Chemistry,* **2007***, 57*, 457-462.

Berselli S. Benitez E., Stefano F. I., Zannoni D., Medici A., Marchetti L. and Fava F. Development and assessment of an innovative soil-washing process based on the use of cholic acid-derivatives as pollutant-mobilizing agents,
Biotechnology and Bioengineering, **2006***,* 93, 761-770.

Boving T., Wang X., and Brusseau M. L. Use of cyclodextrins for the remediation of solvent contaminated porous media, *Groundwater Quality: Remediation and Protection,* **1998***,* 250, 437-440.

Fava F., Ciccotosto V. Effects of randomly methylated-β-cyclodextrins (RAMEB) on the bioavailability and aerobic biodegradation of polychlorinated biphenyls in three pristine soils spiked with a transformer oil, *Applied Microbiology and Biotechnology, Springer-Verlag,* **2002***, 58*, 393-399.

Fenyvesi É., Balogh K., Oláh E., Bátai B., Varga E., Molnár M. and Gruiz K. Cyclodextrins for remediation of soils contaminated with chlorinated organics, *Journal of Inclusion Phenomena and Macrocyclic Chemistry, Springer Netherlands,* **2010**, 1-7.

Fenyvesi É, Gruiz K., Verstichel S., De Wilde B., Leitgib L., Csabai K. et al. Biodegradation of cyclodextrins in soil. *Chemosphere*, **2005**, 6,: 1001-8.

Gan S., Lau E. and Ng H. Remediation of soils contaminated with polycyclic aromatic hydrocarbons (PAHs),
Journal of Hazardous Materials, **2009***,* 172, 532 – 549.

Kania N., Rio S., Monflier E., Ponchel, A. Cyclodextrins adsorbed onto activated carbons: Preparation, characterization, and effect on the dispersibility of the particles in water, *Journal of Colloid and Interface Science,* **2012**, 371, 89 – 100.

Kosaric N. Biosurfactants for soil bioremediation, *Food technology and biotechnology*, **2001**, 39, 295-304.

Leitgib L., Gruiz K., Fenyvesi E., Balogh G., Muranyi A. Development of an innovative soil remediation: "Cyclodextrin-enhanced combined technology", *Science of the Total Environment,* **2008**, 392, 12-21.

McCray J. E., Boving T. and Brusseau M. L. Cyclodextrin-enhanced solubilization of organic contaminants with implications for aquifer remediation, *Winter,* **2000**, 94-103.

McCray J. E. and Brusseau M. L. Cyclodextrin-enhanced in situ flushing of multiple-component immiscible organic liquid contamination at the field scale: mass removal effectiveness. *Environmental Science and Technology*, **1998**, 32, 1285-1293.

Molnár M. Fenyvesi É., Gruiz K, Leitgib L., Balogh G., Murány A. et al. Effects of RAMEB on bioremediation of different soils contaminated with hydrocarbons. *Journal of Inclusion Phenomena and Macrocyclic Chemistry*, **2002**, 44, 447-452.

Molnár M., Leigib L., Gruiz K., Fenyvesi É, Szanisló N., Szejtli J. et al. Enhanced biodegradation of transformer oil in soils with cyclodextrin – from the laboratory to the field. *Biodegradation*, **2005**, 16, 159-168.

Morillo E., Pérez-Martínez J.I., Ginés J.M. Leaching of 2,4-D from a soil in the presence of β-cyclodextrin: laboratory columns experiments. *Chemosphere*, **2001**, 44, 1065-1069.

Rasheed A., Ashok Kumar C.K., Sravanthi V.V.N.N.S. Cyclodextrin as drug carrier molecule: a review. *Scientica Pharmaceutica*, **2008**, 76, 567-598.

Svab M., Kubal M., Müllerova M. and Raschman R. Soil flushing by surfactant solution: Pilot-scale demonstration of complete technology, *Journal of Hazardous Materials,* **2009***,* 163, 410 – 417.

Tick G.R., Lourenso F., Wood A.L., Brusseau M.L. Pilot-scale demonstration of cyclodextrin as a solubility enhancement agent for remediation of a tetrachloroethene contaminated aquifer. *Environmental Science and Technology*, **2003**, 37: 5829-5834.

Valle, E. D. Cyclodextrins and their uses: a review. *Process Biochemistry,* **2004**, 39, 1033 – 1046.

Viglianti, C., Hanna K., Brauer C., Germain P. Removal of polycyclic aromatic hydrocarbons from aged-contaminated soil using cyclodextrins: experimental study. *Environmental Pollution*, **2006**, 140, 427-435.

Wang X. and Brusseau M.L. Solubilization of some low-polarity organic compounds by hydroxypropyl-β-cyclodextrin. *Science and Technology*, **1993**, 27, 2821-2825.

Wong F. and Bidleman T. F. Hydroxypropyl-β-cyclodextrin as non-exhaustive extractant for organochlorine pesticides and polychlorinated biphenyls in muck soil, *Environmental Pollution,* **2010***,* 158, 1303 – 1310.

Zhou W. and Zhu L. Enhanced soil flushing of phenanthrene by anionic/nonionic mixed surfactant, *Water Research,* **2008***,* 42, 101 – 108.